Polyhedron xxx (2017) xxx-xxx

Contents lists available at ScienceDirect

Polyhedron



journal homepage: www.elsevier.com/locate/poly

Employing a neutral " PN_3P " pincer to access *mer*-Re(I) tricarbonyl complexes: Autoionization of a halo ligand and the role of an N-R (R = H, Me) substituent

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ARTICLE INFO

Article history: Received 29 June 2017 Accepted 18 August 2017 Available online xxxx

Keywords: Rhenium Pincer Meridional PNP Autoionization

ABSTRACT

A series of monovalent Re complexes, mer-[Re{ κ^3 -2,6-(Ph₂PNH)₂NC₅H₃}(CO)₃]⁺, cis-[Re{ κ^3 -2,6-(Ph₂PNMe)₂NC₅H₃}(CO)₃]⁺ supported by neutral "PN₃P" ligands have been synthesized by addition of pincer ligand to Re(CO)₅X (X = Cl, Br). The products were characterized by multinuclear NMR and single crystal X-ray diffraction studies and showed a dependence on the identity of the halo ligand in starting material and on the substitution pattern of the pincer ligand. The formation of the *mer*-Re(CO)₃ core geometry and the autoionization of halide ligand in the majority of these species is in marked contrast to the bulk of the literature on the substitution chemistry of Re(I) carbonyl halides.

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1. Introduction

The versatile tridentate architectures provided by pincer ligands have been recognized as an effective means to modify and control the properties of metal complexes from across the periodic table. A common structural motif for this scaffold is organized around a central aromatic backbone with two Lewis base donor groups which are linked to the core with different spacers. Monoanionic versions, with a deprotonated central linker, are one of the most developed class of pincer ligands. There are also a variety of neutral arrangements, often built around central pyridine frameworks and providing "NNN", "PNN", "PNP" and "PN₃P" donor arrays. The design features and applications of the metal complexes of these ligands have been reviewed in relation to their synthesis, their reactivity with small molecule, and catalysis [1–13].

Our initial interest in pincer ligands originated with the application of bis(imino)pyridine scaffolds (a neutral "NNN" framework) to investigate fundamental metal/ligand bonding issues and their ability to provide the appropriate ligand field and coordination geometry to prepare monometallic single molecule magnets [14–22]. With the idea of extending this chemistry and developing new directions we initiated a program to include the neutral

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http://dx.doi.org/10.1016/j.poly.2017.08.020 0277-5387/© 2017 Elsevier Ltd. All rights reserved. ligands derived from the N,N'-bis(diphenylphosphino)-2,6diaminopyridine (**L1**) architecture and their application as pincer ligands [23,24]. We use the notation "PN₃P" in order to differentiate these ligand scaffolds from, for example, di(phosphinomethyl) pyridine, 2,6-{R₂PCH₂}₂(NC₅H₃) ("PNP"), ligands.

N,N'-bis(diphenylphosphino)-2,6-diaminopyridine (**L1**) was first introduced in 1987 with the characterization of neutral carbonyl compounds of group 6 and as complexes of divalent MCl₂ (M = Ni, Pd, Pt) species [25,26]. These researchers also reported an In(III) compound, [2,6-{Ph₂PNH}₂(NC₅H₃)]InCl₃ displaying a ligand with meridional coordination to yield a pseudooctahedral complex [27]. The Kirchner group has made major contributions to this ligand scaffold with variation to both the P-Ph groups and the N-H moieties [28–34]. In particular, we were interested in exploring the application of the N–Me ligand **L2** as this modification would remove a reactive site for deprotonation, introduce a steric load to the ligand and may provide stronger electron donation to a coordinated metal center [28–30,35,36]. The literature for this PN₃P ligand family has been reviewed [5].



The chemistry of rhenium(I) carbonyl complexes is dominated by complexes derived from mono- and disubstitution of Re $(CO)_5 X$ (X = halo ligand). It has been known for nearly 50 years that the common substitution pattern with Re(CO)₅X is sequential replacement of up to two CO groups cis to the halo group thus leading to compounds with a *fac*-tri(carbonyl)Re core [37–40]. It is both interesting and significant that even when potentially tridentate ligands were employed, the formation of bidentate coordination to facial tricarbonyl isomers are the only reported products [41–43]. One of these reports provides tantalizing spectroscopic evidence of the conversion of the bidentate fac-[Re(κ^2 -terpy)Br $(CO)_3$ complex into the *cis*- $[Re(\kappa^3-terpy)Br(CO)_2]$ with CO loss by heating at to 270 °C in the solid state [43]. There is a unique report for the *facial* tridentate coordination of 2,6-bis(pyrazolylmethyl) pyridine ("BPz", Fig. S1) to yield the ionic species fac-[Re(κ^3 -BPz)] $(CO)_3$ ⁺X⁻ starting from the more typical bidentate fac-[Re(κ^2 - $BPz X(CO)_3 X(CO)_3 X = CI, Br, I)$ complex [44].

The recent reports of structurally and spectroscopically characterized complexes of tridentate "NNN" ligand frames, such as terpyridine and bis(imino)pyridine, have stimulated an increasing interest in targeting pincer supported Re(I) carbonyl complexes [45–50]. A common feature of these reports is these syntheses required high temperature reactions in order to get tridentate coordination.

The applications of pyridine-based "PNP" pincer ligands with Re are particularly rare and only recently has the Re(I) chemistry been investigated. Given the strong historical precedent for bidentate ligand coordination, the reaction of Re(CO)₅Cl with 2,6-bis(di-^tbutylphosphinomethyl)pyridine to yield *cis*-[Re(κ^3 -2,6-{^tBu₂-PCH₂₂NC₅H₃)(CO)₂Cl] under rather mild conditions (80 °C/THF) is noteworthy [51]. The non-innocent nature of this ligand frame was exploited for reactions with CO₂ [52]. In that case, the dearomatized ligand, generated by deprotonation of a CH₂ group, was able to participate in reversible CO₂ binding and hydrogenation chemistry. Only three reports for higher oxidation state Re complexes with "PNP" ligands have appeared. A Re(III) complex of this ligand family, mer-[Re(κ^3 -2,6-{Cy₂PCH₂}₂NC₅H₃)Cl₃] has been structurally characterized [53] as have three mixed valent. multiple bonded dirhenium complexes in which the [Re₂]⁵⁺ core has one of the Re centers coordinated to a κ^3 -2,6-{Ph₂PCH₂}₂NC₅H₃ ligand [54]. Finally, some rhenium(V) oxo complexes bearing different bis(R₂phosphinomethyl)pyridine (R = Cy, ^tBu, Ph) ligands have been reported and the non-innocent behavior of the "PNP" ligands discussed [55].

Replacement of one of the PR₂ arms of the "PNP" frame with NEt₂ gives a "PNN" ligand, 2-[(diethylamino)methyl]-6-[(diphenylphosphino)methyl]pyridine. This ligand reacted smoothly with Re(CO)₅X at 110 °C in toluene to yield the Re(I) pincer complexes *cis*-[Re(PNN)(CO)₂X] (X = Cl, Br) analogs of the "PNP" complex [56].

Herein, we report the first Re complexes of N,N'-bis (diphenylphosphino)-2,6-aminopyridine (**L1**) and N,N'-bis (diphenylphosphino)-2,6-(methylamino)pyridine (**L2**). Of particular note is that the PN₃P frameworks yielded tridentate complexes under rather mild conditions compared to the recently reported "NNN" frameworks. The formation of *meridional*-tricarbonyl complexes was dominant and the products of these reactions showed a dependence on the identity of the ligand N-R group as well as the halo group bonded to Re starting material.

2. Results and discussion

Reaction of soluble N,N'-bis(diphenylphosphino)-2,6-aminopyridine ligand (L1) with the Re(I) starting material, Re(CO)₅X (X = Cl, Br), followed the routes outlined in Scheme 1. In the case of X = Cl, this reaction led to the formation of compound **1** in 75% yield. Consistent with this formulation as a *mer*-tricarbonyl species was the appearance of three CO stretching bands at 1911, 1961, 2065 cm⁻¹ in the infrared spectrum of the isolated product. The ³¹P{¹H} NMR spectrum of **1** exhibited a characteristic singlet at 68.8 ppm indicating equivalent P centers within **1** and this chemical shift was reminiscent of that observed for the PNP complex of 2,6-bis(di-tert-butylphosphinomethyl)-pyridine, *cis*-[Re(κ^3 -2,6-{^tBu_2PCH_2}_2NC_5H_3)(CO)₂Cl] [51]. The ¹³C{¹H}NMR of **1** displayed the anticipated two CO signals at δ 190.7 and 198.5 ppm. Finally, the proton NMR spectra showed a characteristic triplet for the *para*-CH for the pyridine at δ 6.85 ppm (³J_{HH}=8.4 Hz). This spectroscopic data pointed to the formation of the complex, *mer*-[Re(κ^3 -2,6-{Ph_2PNH}_2NC_5H_3)(CO)₃]⁺Cl⁻ (**1**) formed by loss of two carbonyl ligands and autoionization to liberate the chloro ligand.

Fortunately, X-ray quality crystals of **1** could be reproducibly obtained and used to confirm the proposed identity and structural features for **1** and these results are summarized in the structural diagram presented in Fig. 1 (Tables S1, S2 and Fig. S2). The structure of **1** confirmed our proposition for the cation as *mer*-[Re(κ^3 -2,6-{Ph₂PNH}₂NC₅H₃)(CO)₃]⁺ and revealed a six-coordinate pseudo-octahedral Re(I) cationic species supported by the tridentate PN₃P pincer ligand and with the coordination environment completed by three *meridional* CO ligands. There are two different environments for the CO ligands with one of them laying in the pseudo-equatorial site of the ligand plane (C(31)–O(2)) and the other two residing in axial sites and *trans* to each other. The chloride counterion, that originated from the Re starting material, was well-separated from the Re-centered cation.

Similar reactivity was observed when the bromo analog, Re $(CO)_5Br$, was employed in the analogous reaction scheme with L1 as shown in Scheme 1 to yield the ionic compound **2**, $[Re(\kappa^3-2,6-\{Ph_2PNH\}_2NC_5H_3)(CO)_3]^*Br^-$. Not surprisingly, compound **2** yielded NMR and IR spectroscopic signatures very similar to **1** which supported our initial formulation. Again, we obtained crystals of **2** which were analyzed by single crystal X-ray analysis and which gave definitive confirmation of a nearly identical connectivity of the cationic Re complex with the non-coordinated anion replace by bromide (Tables S1, S2 and Fig. S3). Complexes **1** and **2** not only represent the first complexes of the "PN_3P" ligand family, they also provide structures that significantly contrast with reported pincer species. In particular, the autoionization of the Re-halo group and more specifically the formation of the *mer*-Re(CO)^{*}_3 core.

In terms of ligand variation, we anticipated that the change of the N-H of the ligand to an N-Me moiety to give **L2** would introduce a steric load to the ligand, may provide stronger electron donation to a coordinated metal center and remove the potentially reactive NH group [28–30,35,36]. Under the same conditions employed for the reaction with **L1**, the reaction of Re(CO)₅Cl was carried out with **L2** to yield complex **3** as shown in Scheme 2. The single ³¹P{¹H} resonance δ = 87.1 ppm suggested a symmetrical coordination environment. The IR spectrum of **3** displayed only two v_{co} at 1834 and 1954 cm⁻¹. These carbonyl carbons appeared in the ¹³C{¹H} NMR at δ 187.8 and 194.5 ppm.

The spectroscopic divergence between **3** and **1** suggested a structural difference for **3**. Colorless crystals of **3** were readily obtained from dichloromethane and the results of a single crystal X-ray analysis are displayed in Fig. 2 (Tables S3, S4 and Fig. S4). The distorted pseudo-octahedral Re coordination environment is constructed from the meridionally coordinated pincer ligand, two *cis*-oriented carbonyl ligands, and a chloro ligand. The chloro group is *cis* to the N_{py} and perpendicular to the PN₃P coordination plane. The two CO ligands reside in different environments with one (C(33)–O(2)) being along the same axis and *trans* to the chloro ligand and the other (C(32)–O(1)) residing in an equatorial site. Complex **3** displays a coordination environment reminiscent of

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Scheme 1.



Fig. 1. Molecular structure of the cation of $[\text{Re}(\kappa^3-2,6-\{\text{Ph}_2\text{PNH}\}_2\text{NC}_5\text{H}_3)(\text{CO}\}_3]^+\text{Cl}^-$, **1.** For clarity, the ligand carbon atoms are rendered in wire frame and hydrogen atoms, other than N-H atoms, have been omitted. Selected bond distances (Å) and angles (°): Re(1)–C(31) 1.921(3), Re(1)–C(32) 1.982(3), Re(1)–C(30) 1.987(3), Re(1)– N(1) 2.174(2), Re(1)–P(1) 2.3659(8), Re(1)–P(2) 2.3706(8), P(1)–Re(1)–P(2) 157.81 (3), C(31)–Re(1)–N(1) 179.33(12).

the "PNP" complex cis-[Re(PNP)(CO)₂Cl] [51] and the "PNN" species cis-[Re(PNN)(CO)₂X] [56].

Attempts to employ **L2** in reaction with Re(CO)₅Br did not follow the route observed with the chloro starting material, rather these reactions followed the pathways shown in Scheme 3. Reaction of equal molar ratio of **L2** and Re(CO)₅Br yielded a colorless product, compound **4**. The ¹H and ³¹P NMR spectroscopy for **4** looked similar to that obtained for **3**. In particular, the appearance of the NMe signal at δ 3.21 ppm as well as the pattern for the aromatic signals and the single ³¹P{¹H} NMR resonance at δ 87.9 ppm indicated some structural similarity for the PN₃P ligand environment of **4** with **3**. However, from the infrared spectrum for **4**, which displayed four carbonyl stretches at 1854, 1931, 1967, and 2063 cm⁻¹, and from the appearance of four signals at δ 185.3, 186.4, 187.3, and 193.6 ppm in the ¹³C NMR, it was clear that **4** was structurally different than **3**.

Crystals of 4 were readily obtained from dichloromethane solutions and single crystal X-ray analysis clarified the constitution of this product as the cation/anion pair mer-[Re(κ^3 -2,6-{Ph₂PNMe}₂- $NC_5H_3(CO)_3$ ⁺[Re(CO)₄Br₂]⁻ as shown in Fig. 3 (Tables S5, S6 and Fig. S5). The cation component of **4** was completely analogous to that observed in 1 and 2 with the replacement of the L1 ligand on the *mer*-Re^I(CO)₃ unit with ligand L2. In 4 the PN₃P ligand is coordinated in a tridentate mode with a meridional arrangement of the three carbonyl groups which can be assigned as one equatorial site, and two axial carbonyl ligands. The anion was an unanticipated part of the product and consists of a pseudo-octahedral Re^I center with cis-oriented bromo groups and four CO ligands. This anion, which can be independently prepared by reaction of Re (CO)₅Br and Br⁻ anion, is well-known in the literature and has been structurally characterized [57-59]. These structural features and the $Re(CO)_4Br_2^-$ anion in particular, explain the additional spectroscopic features associated with the carbonyl groups.

The yield of this reaction is limited due to the fact that the reaction stoichiometry was deficient in $\text{Re}(\text{CO})_5\text{Br}$. Attempts were made to improve the yield by adjusting the reaction stoichiometry to a $\text{Re}(\text{CO})_5\text{Br}$:**L2** ratio of 2:1. Unfortunately, this reaction resulted in isolation of a different product, compound **5**, which was interrogated with NMR and IR spectroscopy. While the ligand-centered spectroscopy of **5** (e.g. ¹H and ³¹P NMR) was nearly identical to that of **4**, the carbonyl signatures obtained by ¹³C NMR and IR spectroscopy showed additional signals. In particular, **5** displayed three ¹³C resonances at 185.8, 187.4, and 193.7 ppm and five v_{CO} peaks in the IR at 1843, 1921, 1965, 1993, 2063 cm⁻¹. On the basis of these



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Fig. 2. Molecular structure of *cis*-[Re{ κ^3 -2,6-(Ph₂PNMe)₂NC₅H₃)(CO)₂Cl], **3.** For clarity, the ligand carbon atoms are rendered in wire frame and hydrogen atoms have been omitted. Selected bond distances (Å) and angles (°): Re(1)–C(32) 1.932 (14), Re(1)–C(33) 1.984(18), Re(1)–N(1) 2.166(12), Re(1)–P(1) 2.332(4), Re(1)–P(2) 2.365(4), Re(1)–Cl(1) 2.505(4), P(1)–Re(1)–P(2) 159.09(13), C(32)–Re(1)–N(1) 177.0 (5).

observations, we anticipated that **5** may be constituted of a cation/ anion pair with an anion possessing Re-carbonyl groups.

We were pleased to obtain crystals of compound **5** that were successfully analyzed by X-ray crystallography and provided the structure for the cationic component displayed in Fig. 4 (Tables S5, S6 and Fig. S6). The cation of **5** displayed the same structural constituents, κ^3 -PN₃P ligation and a meridional orientation for the three carbonyl groups, as observed for **4**. This environment provided a rationalization for three of the ν_{CO} and two of the 13 C signals arising from the *mer*-tricarbonyl structure. The unexpected Re₂(CO)₆(μ -Br)₃⁻ anion provided the source for two of the additional observed ν_{CO} and a third 13 C{¹H} NMR resonance. Once again, although not expected from this reaction, this anion is reported in the literature and has been structurally characterized [60,61]. Interestingly, the initial report for the Re₂(CO)₆(μ -Br)₃⁻ anion involved the reaction of Re(CO)₅Br and toluene to yield an ionic species, [(η^6 -(toluene)Re(CO)₃]⁺Re₂(CO)₆(μ -Br)₃⁻.

Considering the five different pincer products obtained from the reactions of $\text{Re}(\text{CO})_5 X$ (X = Cl, Br) and L1 or L2, it seems that the common route for this reaction is represented by compounds 1, 2, 4, and 5. The four cations obtained in these reactions displayed

the formulae *mer*-[Re(κ^3 -2,6-{Ph₂PNR}₂NC₅H₃)(CO)₃]⁺ (R = H or Me). Furthermore, these four products are logically derived from autoionization of the Re-X function to release halide anions which either functioned as counterions, in the case of 1 and 2, or apparently reacted further with starting material to yield halide substituted rhenium carbonyl anions of **4** (e.g. $Re(CO)_4Br_2^-$) and **5** (e.g. $\text{Re}_2(\text{CO})_6(\mu-\text{Br})_3^-$). In these four cases, the reaction proceeds along a unique path to yield pincer-supported mer-(tricarbonyl)Re(I) complexes unprecedented in the literature. In contrast to these reactions, the reaction of L2 and Re(CO)₅Cl apparently followed a different and more conventional pathway to yield cis-[Re(κ^3 -2,6-{Ph₂PNMe}₂NC₅H₃)(CO)₂Cl], **3**. This complex is the "PN₃P" analog of $[\text{Re}(\kappa^3-\text{PNP})\text{Cl}(\text{CO})_2]$ [51] and $[\text{Re}(\kappa^3-\text{PNN})\text{X}(\text{CO})_2]$ [56]. These three species would appear to have followed a reaction pathway that is consistent with the large body of literature for substitution reactions of Re(CO)₅X. Namely, the initial formation of a bidentate "fac-LRe(CO)₃X" via the substitution reactions of two CO ligands cis to the Br group [37–40]. The third pincer arm would then coordinate through substitution of a third CO that is also cis to the Br ligand with the resulting complexes exhibiting analogous coordination environments.

With the goal of gaining an understanding of the origin of the different observations for the reactions of $\text{Re}(\text{CO})_5\text{Cl}$ versus Re $(\text{CO})_5\text{Br}$ with **L2**, we performed a DFT optimization on complex **3** and the cationic complex *mer*-Re(κ^3 -2,6-{Ph}_2\text{PNMe}}₂NC₅H₃)(CO)⁺₃ using the B3LYP functional and a mixed basis set of LANL2DZ for Re, DZVP for Br and TZVP for the remaining atoms. The optimized structures were an excellent match to the experimental structures indicating that they represent good models for this chemistry (Tables S7–S9). In order to make a thermodynamic comparison between *mer*-[Re(κ^3 -2,6-{Ph}_2\text{PNMe}}(CO)₃]⁺[Re(CO)₄X₂]⁻ (X = Cl, Br) and *cis*-[Re(κ^3 -2,6-{Ph}_2\text{PNMe}}(CO)₂Cl], we optimized and carried out frequency calculations on all of the complexes in the following set of balanced equations:

$$\frac{cis[\text{Re}(\kappa^{3}-2, 6-\{\text{Ph}_{2}\text{PNMe}\}_{2}\text{NC}_{5}\text{H}_{3})(\text{CO})_{2}\text{Cl}] + \text{Re}(\text{CO})_{5}\text{Cl} \rightarrow \\ mer-\text{Re}\{\kappa^{3}-2, 6-(\text{Ph}_{2}\text{PNMe})_{2}\text{NC}_{5}\text{H}_{3}\}(\text{CO})_{3}^{+} + \text{Re}(\text{CO})_{4}\text{Cl}_{2}^{-}$$
(1)

$$cis-[\text{Re}(\kappa^{3}-2, 6-\text{Ph}_{2}\text{PNMe}_{2}\text{NC}_{5}\text{H}_{3})(\text{CO})_{2}\text{Br}] + \text{Re}(\text{CO})_{5}\text{Br} \rightarrow \\mer-\text{Re}\kappa^{3}-2, 6-(\text{Ph}_{2}\text{PNMe})_{2}\text{NC}_{5}\text{H}_{3}(\text{CO})_{4}^{+} + \text{Re}(\text{CO})_{4}\text{Br}_{2}^{-}$$
(2)

These DFT optimizations were carried out using the B3LYP functional and the same mixed basis set (LANL2DZ, DZVP and TZVP). In addition, we employed the PCM formalism within Gaussian 09 using tetrahydrofuran as the solvent. The goal here was to try to



Please cite this article in press as: G.K. Rao et al., Polyhedron (2017), http://dx.doi.org/10.1016/j.poly.2017.08.020



Fig. 3. One of the two cations of the molecular structure for *mer*-[Re(κ^3 -2,6-{Ph₂-PNMe}₂NC₅H₃)(CO)₃][Re(CO)₄Br₂] (**4**). For clarity, the ligand carbon atoms are rendered in wire frame and the anion and hydrogen atoms have been omitted. Selected bond distances (Å) and angles (°): Re(2)–C(67) 1.925(8), Re(2)–C(66) 1.991 (10), Re(2)–C(68) 1.997(9), Re(2)–N(4) 2.169(6), Re(2)–P(4) 2.3396(17), Re(2)–P(3) 2.3608(18), C(67)–Re(2)–N(4) 176.5(3), P(4)–Re(2)–P(3) 158.99(7).



Fig. 4. Structure of the cation portion of *mer*-[Re(κ^3 -2,6-{Ph₂PNMe}₂NC₅H₃)(CO)₃] [Re₂(CO)₆(µ-Br)₃] (**5**). For clarity the ligand carbon atoms are rendered in wire frame representation and anion and hydrogen atoms are omitted. Selected bond distances (Å) and angles (°): Re(1)–C(33) 1.928(6), Re(1)–C(34) 1.979(6), Re(1)–C(32) 1.990(7), Re(1)–N(1) 2.171(4), Re(1)–P(2) 2.3511(15), Re(1)–P(1) 2.3677(16), C (33)–Re(1)–N(1) 178.0(2), P(2)–Re(1)–P(1) 157.44(6).

understand a potential thermodynamic origin for the observation of divergent reactions of **L2** with Re(CO)₅X (X = Cl, Br). It is important to realize that like the two bromo anions observed with **4** (e.g. Re(CO)₄Br₂) and **5** (e.g. Re₂(CO)₆(μ -Br)₃), both Re(CO)₄Cl₂ [58] and Re₂(CO)₆(μ -Cl)₃ [60,62] are known in the literature and the dirhenium anion has been structurally characterized. Table 1 provides the computed free energies for the compounds in Eqs. (1) and (2). Both Eqs. (1) and (2) gave small negative ΔG values of -0.00195 Hartree (i.e. -1.22176 kcal/mol) for Eq. (1) and -0.00587 Hartree (i.e. -3.68348 kcal/mol) for Eq. (2). It would thus annear that formation of the cation (anion pair ac was characterized).

appear that formation of the cation/anion pair, as was observed in the case of formation of compound **4**, are slightly favored thermodynamically for both the chloro and bromo species. Since these computed values for ΔG are quite small, it is possible that the products are in fact not favored for the chloro complex or that kinetic factors have played a role in the observed products. Interestingly, although reported, there are no reported structurally characterized Re(CO)₄Cl₂⁻ compounds. In conclusion, we have successfully applied two "PN₃P" ligands to support five new Re(I) carbonyl species thus providing the first application of this ligand family in Re chemistry. The dominant products of this chemistry are pincer ligated cations, *mer*-Re(κ^3 -2,6-{Ph₂PNR}₂NC₅H₃}(CO)⁺₃, that result from an autoionization of the Re-X (X = Cl, Br) of the starting material. The reaction pathway remains a part of our ongoing investigations; however, it seems clear that this substitution does not follow the conventional route of preferential substitution of ligands *cis* to the Re-X group that is dominant in the literature. The influence of both the identity of the halo ligand in the Re(CO₅X (X = Cl, Br) starting material and the NR substituent is part of our continuing examination of this chemistry.

3. Experimental

3.1. General procedures

Reagents were purchased from Strem Chemicals and used as received. Analytical grade solvents were purchased from Aldrich and used as received.

3.2. X-ray crystallography

Data collection results for compounds **1–5** represent the best data sets obtained in several trials for each sample. The crystals were mounted on thin glass fibers using paraffin oil. Prior to data collection crystals were cooled to 200(2) °K. Data were collected on a Bruker AXS SMART single crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) APEX II CCD detector. Raw data collection and processing were performed with APEX II software package from BRUKER AXS [63].

Diffraction data for samples 1, 3, and 5 were collected with a sequence of 0.3° ω scans at 0, 120, and 240° in φ . Due to lower unit cell symmetry in order to ensure adequate data redundancy, diffraction data for 2 and 4 were collected with a sequence of $0.3^{\circ} \omega$ scans at 0. 90, 180 and 270° in ω . Initial unit cell parameters were determined from 60 data frames with $0.3^{\circ} \omega$ scan each collected at the different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied [64]. Systematic absences in the diffraction data-set and unit-cell parameters were consistent with triclinic P-1 (No2) for compounds **2** and **4**, monoclinic $P2_1/c$ (No14) for compounds **3** and **5**, monoclinic $P2_1/n$ (No14, alternative settings) for compound 1. Solutions in the centrosymmetric space groups for all compounds yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2 .

Structural model for **2** contains one molecule of positively charged Re complex, one bromine counter-anion and one crystallization water molecule. All fragments are located in the general positions.

Structure of **4** reveals two Re containing target molecules and two "ReBr₂" counter-anions per unit cell. Large residual electron density peaks were refined as partially occupied (37%) methanol molecule and three water solvent molecules (54%, 35%, 46%) based on the synthesis information. Occupancy of the solvent molecules were allowed to refine on the initial stages of the refinement but were fixed for the final refinement cycles to obtain constant unit cell atomic content.

For compound **5** the structure consisted of one Re target compound molecule and one "Re₂Br₃" counter anion. Both structural fragments are located in the general positions of the unit cell.

The sample for **3** was contaminated by considerable amount of microcrystalline material. Structural data set was showing visible

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Table 1

Tabulated values for the sum of electronic and thermal free energies (Hartree) for the compounds in Eqs. (1) and (2). Optimizations were carried out using the default THF solvent parameters with the PCM model in Gaussian 09.

Compound	$Re(PN_3P)(CO)_2X$	Re(CO) ₅ X	$Re(PN_3P)(CO)_3^+$	$Re(CO)_4X_2^-$
X = Cl	-2812.026646		-2464.985970	-1453.413902
X = Br	-4925.495978		-2464.985970	-5680.361295

amount of the diffraction intensities that could not be attributed to the proposed space group. The data set was tried for non-merohedral and pseudo-merohedral twinning. However no reasonable transformation matrixes were discovered. The obtained data set was integrated using only one unit cell and the structure was solved for non-twinning model. Due to unaccounted reflections intensities it was necessary to apply thermal constrains (SIMU, RIGU) of the anisotropic refinement stages to ensure acceptable values of thermal motion parameters for non-hydrogen atoms. Structural model for **3** consists of one molecule of Re compound located in the general position of the unit cell.

Structural solution for **1** compound reveals one molecule of Re target species and one chlorine counter-anion. Both fragments are located in the general positions of the unit cell. It was attempted to interpret residual electron density peaks with the values of 0.99 e as a possible crystallization solvent. However, such attempts were unsuccessful without considerable amount of geometrical restrains, therefore the solvent fragments were omitted from the final refinement of the structural model.

All non-hydrogen atoms in structural models of all compounds were refined with the full set of anisotropic thermal motion parameters. For all the compounds hydrogen atoms positions were initially assigned based on geometry of bearing non-hydrogen atoms. After initial placement all hydrogen atoms were treated as idealized contributions during the refinement. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12 [65].

4. Computational details

Density functional theory (DFT) calculations have been performed using the Gaussian 09 package [66]. The structures of all species were optimized using the B3LYP exchange–correlation functional with the LanL2DZ basis set for Re, the DZVP basis set for Br and the all-electron TZVP basis set for C H N P Cl. Computations were performed on complexes solvated with THF using the integral equation formalism variant of PCM, with the default parameters for tetrahydrofuran.

4.1. Synthesis of N,N'-bis(diphenylphosphino)-2,6-diaminopyridine (L1)

The ligand was synthesized by the slight modification of known procedure [25,26]. 2,6-Diaminopyridine (2.18 g, 20 mmol), dissolved in 40 mL dry THF, was cooled on ice-salt bath under N2 atmosphere. A solution of chlorodiphenylphosphine (9.24 mL, 42 mmol) in 10 mL THF was added. Triethylamine (44 mmol, 4.5 g) was dropwise added to the reaction mixture. The resulting reaction mixture was stirred for 2 h at room temperature and refluxed for 16 h. The solution was cooled to room temperature and filtered twice with a frit containing Celite under N₂ atmosphere. The solvent of resulting reaction mixture was removed under vacuum which was further washed with dry hexane $(3 \times 50 \text{ mL})$ yielding colorless solid. Yield: 7.25 g (76%). NMR: ¹H (300 MHz, CDCl₃, 25 °C, TMS): δ (ppm): 5.02 (d, 2H, NH, *I* = 8.3 Hz), 6.50 (d, 2H, *I* = 8.3 Hz), 7.33–7.38 (m, 12H), 7.45–7.49 ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C): δ = 99.0 (t, (m, 9H).

J = 16.0 Hz), 128.5 (t, *J* = 6.6 Hz), 121.1, 131.3 (d, *J* = 21 Hz), 139.3, 139.8, 157.5 (dd, *J* = 2 & 21.0 Hz). ${}^{31}P{}^{1}H{}$ (121 MHz, CDCl₃, 25 °C, H₃PO₃): δ (ppm): 25.9.

4.2. Synthesis of N,N'-dimethyl-2,6-diaminopyridine

2,6-Dibromopyridine (10.0 g, 42.2 mmol) was stirred with 40 mL methylamine (40% solution in water) at 200 °C for 20 h in a sealed tube. The solution was cooled and mixed with 100 mL water. The aqueous layer was then extracted with chloroform twice. The chloroform layer was dried over sodium sulphate. The solvent was evaporated off under reduced pressure on a rotary evaporator to get dark red colored compound which was further purified by column chromatography using a mixture of ethylacetate and hexane followed by dichloromethane. Yellow solid. Yield: 4.91 g (85%). NMR: ¹H (400 MHz, CDCl₃, 25 °C, TMS): δ (ppm): 2.85 (d, 6H, Me, *J* = 5.2 Hz), 4.40 (bs, 2H, NH), 5.74 (d, 2H, *J* = 7.9 Hz), 7.29 (t, 1H, *J* = 7.9 Hz) [67].

4.3. Synthesis of N,N'-bis(diphenylphosphino)-N,N'-methyl-2,6diaminopyridine (**L2**)

The ligand was synthesized by the slight modification of known procedure [28]. Butyllithium (2.5 M in hexane, 8.0 mmol, 3.2 mL) was dropwise added to a toluene (100 mL) solution of N,N'dimethyl-2,6-diaminopyridine (1.0 g, 7.3 mmol) cooled on ice-salt bath. The mixture was stirred at room temperature for 2 h. It was then cooled to -78 °C using dry ice-acetone bath and 1.3 mL (7.3 mmol) of chlorodiphenylphosphine was added. The resulting reaction mixture was stirred for 2 h at room temperature and refluxed for 18 h. The solution was cool to room temperature and filtered twice with a frit containing Celite under N₂ atmosphere. The above procedure was repeated with the yellow solution. The resulting reaction mixture was filtered and solvent was removed under vacuum yielding yellow oil. This oil was refluxed in acetonitrile for 10 min which on cooling at room temperature results in the white precipitate. Acetonitrile was decant and compound was dried under vacuum. Yield: 1.70 g (46%). NMR: ¹H (300 MHz, CDCl₃, 25 °C, TMS): δ (ppm): 2.85–2.86 (m, 6H, CH₃), 6.82 (d, 2H, J = 7.9 Hz, 7.32–7.42 (m, 21H). ³¹P{¹H} (121 MHz, CDCl₃, 25 °C, H₃PO₃): δ (ppm): 49.5.

4.4. $[Re\{2,6-(Ph_2PNH)_2NC_5H_3\}(CO)_3]^+$ Br⁻/Cl⁻ 1 and 2

Ligand (0.187 g, 0.393 mmol), $\text{Re}(\text{CO})_5\text{Br}$ $(0.159 \text{ mg}, 0.393 \text{ mmol})/\text{Re}(\text{CO})_5\text{Cl}$ (0.141 mg, 0.393 mmol) and a stir bar were added in a 100 mL round bottom flask containing 20 mL dry THF in glove box. The solution was taken out and refluxed for 4 h under N₂ atmosphere. Solvent was concentrated to 5 mL and 50 mL hexane was added to precipitate a solid which was filtered and dried under vacuum give complexes. Crystallization was carried out in dichloromethane/hexane mixtures.

4.5. [Re{2,6-(Ph₂PNH)₂NC₅H₃}(CO)₃]Cl (1)

Yield (0.218 g, 75.4%); ¹H NMR (400 MHz, CD₂Cl₂, 25 °C): 6.85 (t, 1H, *J* = 8.4 Hz), 7.25–7.38 (m, 14H), 7.86–7.98 (m, 8H), 11.4

(s, 2H). ¹³C{¹H} NMR (100 MHz, DMSO, 25 °C): 103.8, 131.7, 133.5 (t, J = 6.3 Hz), 134.3, 139.4 (t, J = 29.6 Hz), 143.7, 164.6 (t, J = 7.5 Hz), 190.7, 198.5. ³¹P{¹H} NMR (161 MHz, CD₂Cl₂, 25 °C): 68.8. HR-MS (CH₃CN): [M–Cl] m/z 746.0909; calcd value for C₃₂-H₂₅N₃O₃P₂Re 746.0901 (δ 1.1). Infrared data (cm⁻¹): 589, 609, 633, 690, 701, 740, 798, 853, 895, 998, 1051, 1102, 1171, 1187, 1219, 1305, 1335, 1397, 1469, 1575, 1613, 1911, 1961, 2065, 2725, 2766, 2813, 2988.

4.6. $[Re\{2,6-(Ph_2PNH)_2NC_5H_3\}(CO)_3]Br(2)$

White powder. Yield 0.194 g (66.9%); ¹H NMR (400 MHz, CD₂-Cl₂, 25 °C): 6.92 (t, 1H, *J* = 7.8 Hz), 7.30–7.40 (m, 12H), 7.41 (d, 2H, *J* = 7.88 Hz), 7.89–7.93 (m, 8H), 10.6 (s, 2H, NH). ¹³C{¹H} NMR (100 MHz, DMSO, 25 °C): δ = 101.3, 128.8 (t, *J* = 23.3Hz), 130.8 (t, *J* = 29.6Hz), 131.6, 136.3 (t, *J* = 29.9 Hz), 140.1, 161.7 (t, *J* = 9.5 Hz), 187.9, 195.2. ³¹P{¹H} NMR (161 MHz, CD₂Cl₂, 25 °C): δ = 68.0. HR-MS (CH₃CN): [M–Br] *m*/*z* 746.0934; calcd value for C₃₂H₂₅N₃O₃P₂-Re 746.0901 (δ 4.4). Infrared data (cm⁻¹): 589, 609, 633, 690, 701, 740, 798, 853, 895, 998, 1051, 1102, 1171, 1187, 1219, 1305, 1335, 1397, 1436, 1469, 1575, 1613, 1912, 1961, 2065, 2718, 2889, 2994.

4.7. Synthesis of [Re{2,6-(Ph₂PNMe)₂NC₅H₃}(CO)₂Cl] (**3**)

A solution of ligand **L2** (0.101 g, 0.2 mmol) was made in 15 mL of tetrahydrofuran. Re(CO)₅Cl (0.072 g, 0.2 mmol) was added via stirring to the THF solution of ligand in glove box. The mixture was further stirred for 2 h at 100 °C. The colorless solution was cooled and the volume was reduced to ~5 mL under vacuum. Addition of excess hexane resulted in the formation of a colorless powder. Single crystals of **3** were grown from a dichloromethane/hexane solution.

3; Yield 0.101 g (65%); ¹H NMR (300 MHz, DMSO, 25 °C): $\delta = 3.14$ (s, 6H, CH₃), 6.87 (d, J = 8.4 Hz, 2 H), 7.61–7.70 (m, 20H), 8.09 (t, J = 8.4 Hz, 1H). ¹³C{¹H} NMR (75 MHz, DMSO, 25 °C): $\delta = 37.3$ (s, CH₃), 102.5, 129.5 (t, J = 5.4 Hz), 130.5 (t, J = 6.7 Hz), 132, 132.1 (t, J = 28.6 Hz), 142.2, 164.5 (t, J = 9.4 Hz), 187.8, (t, J = 10.6 Hz), 194.5. ³¹P{¹H} NMR (121 MHz, DMSO, 25 °C): $\delta = 87.1$. HR-MS (CH₃CN): [M–Cl+CH₃CN] m/z 787.1495; calcd value for C₃₅H₃₂N₄O₂P₂Re 787.1530 (δ –4.5). Infrared data (cm⁻¹): 573, 598, 611, 658, 692, 714, 738, 787, 866, 950, 999, 1074, 1103, 1141, 1177, 1249, 1295, 1350, 1427, 1459, 1474, 1565, 1593, 1834, 1954, 3089.

4.8. [RePNP(CO)₃]·Re(CO)₄Br₂ (4), [RePNP(CO)₃]·Re₂(CO)₆Br₃ (5)

A solution of ligand **L2** (0.101 g, 0.2 mmol) was made in 15 mL of tetrahydrofuran Re(CO)₅Br (0.0.081 g, 0.2 mmol in case of **4**/0.162 g, 0.4 mmol in case of **5**) was added via stirring to the THF solution of ligand in glove box. The mixture was further stirred for 2 h at 100 °C. The colorless solution was cooled and the volume was reduced to ~5 mL under vacuum. Addition of excess hexane led to formation of colorless powders. Single crystals of **4** and **5** were grown from dichloromethane/hexane solutions.

4; Yield 0.098 g (40%); ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 3.21 (t, *J* = 2.6 Hz, 6 H, CH₃), 6.86 (d, *J* = 8.4 Hz, 2H), 7.58–7.60 (m, 20H), 8.13 (t, *J* = 8.3 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃, 25 °C): δ = 37.7 (s, CH₃), 102.7 (t, *J* = 3.3 Hz), 129.6 (t, *J* = 5.5 Hz), 130.5 (t, *J* = 6.6 Hz), 132.0 (t, *J* = 28.5 Hz), 132.1, 143.2, 161.6 (t, *J* = 9.3 Hz), 185.3, 186.4, 187.3 (t, *J* = 9.1 Hz), 193.6. ³¹P{¹H} NMR (162 MHz, CDCl₃, 25 °C): δ = 87.9. HR-MS (CH₃CN): [M–Re(CO)₄-Br₂] *m*/*z* 774.1222; calcd value for C₃₄H₂₉N₃O₃P₂Re 774.1214 (δ 1.0). Infrared data (cm⁻¹): 583, 611, 638, 693, 739, 779, 866, 950, 997, 1050, 1073, 1097, 1141, 1178, 1252, 1297, 1355, 1397, 1434, 1463, 1575, 1596, 1854, 1931, 1967, 2063, 2972. **5**; Yield 0.140 g (45%); ¹H NMR (400 MHz, CDCl₃, 25 °C): $\delta = 3.19$ (t, J = 2.8 Hz, 6H, CH₃), 6.93 (d, J = 8.0 Hz, 2H), 7.51–7.55 (m, 20H), 8.13 (t, J = 8.3 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃, 25 °C): $\delta = 37.8$ (s, CH₃), 103.0 (t, J = 3.3 Hz), 129.6 (t, J = 5.5 Hz), 130.5 (t, J = 6.7 Hz), 132.1 (t, J = 28.5 Hz), 132.1, 143.5, 161.6 (t, J = 9.3 Hz), 185.8, 187.4 (t, J = 8.9 Hz), 193.7. ³¹P{¹H} NMR (162 MHz, CDCl₃, 25 °C): $\delta = 88.6$. HR-MS (CH₃CN): [M–Re(CO)₆-Br₃] m/z 774.1171; calcd value for C₃₄H₂₉N₃O₃P₂Re 774.1214 (δ –5.5). Infrared data (cm⁻¹): 586, 612, 637, 650, 693, 741, 778, 867, 951, 996, 1050, 1098, 1142, 1181, 1252, 1292, 1350, 1397, 1422, 1434, 1459, 1575, 1601, 1843, 1921, 1965, 1993, 2063, 3052.

Acknowledgement

We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for funding.

Appendix A. Supplementary data

CCDC 1558915-1558919 contains the supplementary crystallographic data for **1–5**. These data can be obtained free of charge via http://dx.doi.org/10.1016/j.poly.2017.08.020, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. poly.2017.08.020.

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Please cite this article in press as: G.K. Rao et al., Polyhedron (2017), http://dx.doi.org/10.1016/j.poly.2017.08.020

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